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(54) IMPROVEMENTS IN OR RELATING TO METHODS
 AND COMPOSITIONS FOR NUCLEATING ALPHA-OLEFIN
 POLYMERS

(71) We, DART INDUSTRIES INC. (formerly Rexall Drug and Chemical Company), a Corporation organised and existing under the laws of the State of Delaware 5 United States of America, of 8480, Beverly Boulevard, Los Angeles, State of California, 90054, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method 10 by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods and compositions for modifying the physical characteristics of crystalline alpha-olefin polymers.

It is well known that the crystallite size as well as the percentage of crystallinity influence the properties of crystalline alpha-olefin polymers, such as polypropylene. In general, commercial processes for the preparation of homopolymers of propylene are carried out under conditions which favour the production of crystalline polypropylene by the use of titanium catalysts activated with aluminium alkyl. The polymer produced because of its crystalline content has various desirable physical properties such as stiffness and tensile strength.

Crystalline polypropylene as employed in the present Specification means solid polypropylene resins having a high degree, at least 30% and preferably 50%, of crystallinity determined by X-ray analysis or other standard method. In general, polyalpha-olefins 30 having a crystallinity of this order contain at most small portions of material which are extractable in non-aromatic hydrocarbons. Typically, the proportion of highly crystalline polypropylene which is extractable in boiling heptane or isoctane is less than 25% and usually less than 10%. Similarly, "crystallizable" polymers are those which have a molecule arrangement that enables them to solidify from a melt in a highly crystalline structure. 40 The general practice in the art is to refer to "crystalline" or "crystallizable" polymers 45

rather than "partially crystalline" or "partially crystallizable" polymers even though alpha-olefin polymers of 100 percent crystal structure are not known to exist. For example, a crystallinity of 70% is extremely high for polypropylene.

Normally solid, crystalline polypropylene usually has a viscosity average molecular weight of at least about 40,000 and generally between 100,000 and 1,200,000. For convenience the molecular weight is usually expressed in terms of intrinsic viscosity. The intrinsic viscosity of polypropylene, measured in decalin at 150°C, is generally between 1.0 and 6 dl./g. but may be as low as 0.5 or less and as high as 10 or more.

A serious commercial disadvantage of crystalline polypropylene which will be referred to for the purpose of this discussion is the lack of clarity or transparency which shows up as haze in thin films and as translucency, decreasing to ultimate opacity, in polypropylene articles of increased thickness. Studies have revealed that polypropylene crystallizes from a melt in a form in which the individual crystals are present in spheroid or ellipsoid bodies, known as spherulites, and that clarity or transparency are markedly improved when the spherulites are relatively small. Therefore, it has been proposed to add a variety of materials to polypropylene in order to control the rate of growth and therefore the size of the crystallites or spherulites. By modifying the crystallization process, that is, by nucleation of the polymers in such a manner significant improvements are realised in physical properties such as clarity, transparency, stiffness, hardness and density in some cases.

Alkali metal benzoates, particularly sodium benzoate, have been suggested heretofore as additives for modifying the crystallization process of crystalline alpha-olefin polymers. For most purposes, minute amounts of alkali metal benzoates have been very effective in modifying the crystallization process and the crystal

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structure of polypropylene. Unfortunately the use of commercially available forms of alkali metal benzoates as well as other nucleating agents have the disadvantage of producing

5 polypropylene containing noticeable amounts of non-dispersed additive. This undesirable result is attributed to the limited solubility of most of the more effective nucleating agents and to the unfavourable particle size distribution of their commercial forms.

It has now been found that the dispersion problems associated with the use of nucleating agents for modifying the physical properties of crystalline alpha-olefin polymer can be

15 readily overcome by preparing an alpha-olefin polymer masterbatch containing a nucleating agent under carefully controlled conditions, and mixing the masterbatch with an alpha-olefin polymer.

20 Accordingly, the present invention provides a masterbatch blend comprising from 95% to 25% by weight of a crystalline alpha-olefin polymer and, substantially uniformly dispersed therein, from 5% to 75% by weight of a water-soluble oxygen-containing nucleating agent.

The invention also provides a process for preparing a masterbatch blend of a crystalline alpha-olefin polymer and, substantially uniformly dispersed therein, a water-soluble oxygen-containing nucleating agent, which process comprises dissolving the nucleating agent in water, precipitating a gel-like slurry by admixing the solution of the nucleating agent in water with an excess amount of a non-solvent, with which water is at least partially miscible, for the nucleating agent, adding particles of a crystalline alpha-olefin polymer to the slurry, agitating to disperse the polymer particles in the slurry, and separating the solids from the resulting polymer-containing slurry.

Although the masterbatch and the process for its preparation will be hereinafter more particularly described and illustrated with reference to the use of an alcohol, as the non-solvent, and sodium benzoate, as the preferred nucleating agent, it will be understood that other non-solvents and nucleating agents and other alkali metals such as lithium, potassium, and the like as well as mixtures thereof or mixtures of nucleating agents with sodium benzoate can also be effectively utilised.

55 The modification of the properties of crystalline polypropylene and copolymers thereof are of particular interest and emphasis will be placed on the use of such polymers. The properties of importance which are 60 benefited by the nucleating agents are increased clarity for thin films, stiffness (for copolymers also), hardness and density. By nucleating agents it is meant those acids or their salts effective in reducing spherulite size.

The masterbatch of this invention is generally prepared by dissolving the nucleating agent, such as sodium benzoate, in water, combining the resulting solution with excess alcohol to form a gel-like slurry, admixing polymer particles, for example finely-divided powder, with the slurry with agitation to ensure thorough mixing, separating the solids from the resulting polymer-containing slurry, for example by filtration or centrifugation. The thus produced masterbatch will generally contain the nucleating agent, such as sodium benzoate, in an amount ranging from 5 to 75%, usually from about 25 to 50% by weight, and preferably about 30 to 40% by weight, based on the total weight of the masterbatch composition.

70 The preparation of the masterbatch may be carried out under ambient temperature and pressure conditions. If desired, elevated temperatures of from about 30° to 100°C may be employed.

75 The solids separated from the polymer-containing slurry may be dried at an elevated temperature, for example from about 20° to 60°C. It is preferred to effect drying under vacuum conditions or where the pressure is reduced to at least 15 inches of Hg.

80 Advantageously, the amount of nucleating agent dissolved in water should be sufficient to give a concentration just below the saturation point, i.e., in the case of sodium benzoate approximately 61 grams per 100 grams of water at 25°C. It will be understood, however, that lower concentrations of sodium benzoate can also be effectively employed. Thus saturation can be considered as 100 percent concentration in this case and in general concentrations of the nucleating agent of from 10 to 90% plus are preferred.

85 The alcohol used in forming the gel-like slurry may contain from 1 to 10 carbon atoms, for example methanol, ethanol, isopropanol, propanol, pentanol or hexanol, or a mixture thereof. Preferred alcohols include isopropanol and methanol. The essential characteristics of the alcohol employed in this dispersion step is that it be easily removed during drying, that is, it has a high vapour pressure. The amount of alcohol employed may vary over a wide range, 10 to 200 times the volume of the aqueous solution, and the exact amount of alcohol employed is not critical. In general, however, a sufficient amount of alcohol is admixed with the aqueous solution of the nucleating agent to permit thorough and complete mixing of the polymer added to the slurry when subjected to agitation. If necessary, additional alcohol can be added to the admixture during agitation to ensure an adequate dispersion of the nucleating agent in the polypropylene.

90 Although alcohol has been specified above as the preferred component, other non-solvents for the nucleating agent can be used

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such as oxygenated organic compounds of which ketones for example (acetone), esters or partial esters, glycols, such as ethylene glycol, and aldehydes are representative.

- 5 Water is required as the solvent for the nucleating agent and an oxygenated organic compound such as an alcohol as the non-solvent. The other requirement to be met in accordance with this invention is that
 10 the water must be partially, but preferably substantially completely, miscible with the alcohol.

In the process of this invention it is the above prerequisites that result in the formation of the gel when alcohol is added to the water containing the nucleating agent dissolved therein. The nucleating agent in the "precipitated" form in the gel is of very fine particle size probably approaching colloidal
 20 form. In this form the nucleating agent can readily be incorporated into a polyolefin, that is, it promotes solubility in the polymer thereby becoming extremely effective in its function as a nucleating agent.

- 25 In the process of this invention it is not always necessary to have a nucleating agent that has a melting point above the crystalline alpha-olefin polymer, or a salt of such an agent. Some effective substances, such as
 30 benzoic acid, are good nucleating agents. What is required of a good nucleating agent, whether it be a liquid or solid or a salt, is that it will form micro-ordered regions in the polymer melt which will initiate the crystallization.

35 The nucleating agents which have been tested for this function and found (in this case and in the literature) to yield desirable results include the sodium salts of benzoic acid, sodium glutarate, sodium adipate, sodium succinate and the lithium salts thereof, and the sodium salt of crotonic acid. In general, nucleating agents include mono and disodium salts of aromatic and/or aliphatic mono and
 40 dicarboxylic acids and alkyl derivatives such as t-butyl sodium benzoate, ortho methyl benzoic acid, 2,4-dimethyl benzoic acid and alpha naphthoic acid. One of the nucleating agents discovered during experimentation on such agents which is new and extremely effective is the trans acid salt of cinnamic acid.

The crystalline alpha-olefin polymers can be treated with nucleating agents in amounts
 55 of from 0.05% to 2.0% by weight, preferably 0.1% to 1.0% by weight, in order to realise the benefits of the incorporated additives. The polymers which can be treated include homopolymers of ethylene, propylene,
 60 4 - methyl - pentene - 1, butene - 1, 3-methylbutene - 1 and pentene - 1, and random or block copolymers of propylene with ethylene, 4 - methylpentene - 1, 3 - methylbutene - 1 or pentene - 1. Block copolymers of ethylene
 65 and another alpha-olefin can be particularly

benefited (stiffness increase) by the nucleating agents herein.

Conventional equipment and procedures may be utilised for accomplishing the mixing of the polymer particles with the aqueous, gel-like slurry. Illustrative equipment includes the ball mill, Waring Blender and various mixers. In general the blades or paddles will be rotated at a rate of from about 5 to 200 RPM, although the rate of degree of agitation is not critical provided that complete dispersion is attained. Agitation may either be commenced prior to, during or following the addition of the polymer particles to the gel-like slurry containing water, alcohol and sodium benzoate. As previously discussed, the amount of polymer added may be sufficient to give a final masterbatch composition containing about 25 to 50%, preferably about 30 to 40%, sodium benzoate with the remainder being polymer. It is also possible to prepare polypropylene masterbatches (or masterbatches of other olefin polymers) according to above described process which contain other conventional additives in addition to the sodium benzoate. Such other additives include, for example, antioxidants, stabilizers against ultraviolet radiation, fillers, slip agents and antistats, as well as mixtures thereof.

90 After the addition of polymer and agitation has been completed, the resulting polymer-containing slurry is treated to separate solids therefrom. Conventional solids separating equipment and techniques can be employed in this step, for example drum filters and centrifuges. For most purposes centrifugation is the preferred procedure for commercial operations.

95 The resulting solids comprising polymer and sodium benzoate are preferably dried at elevated temperatures to remove residual water and alcohol, if present. As hereinbefore described, the drying is preferably carried out under vacuum conditions and at a temperature ranging from 20° to 60°C, preferably 30° to 60°C. The drying step may either take place in the centrifuge or other separatory equipment or after the solids have been removed therefrom.

100 The polypropylene or other olefin polymers employed in the above described process are those produced by polymerising in the presence of stereospecific catalyst systems. Such catalyst systems are generally transition metal halides, for example titanium trichloride, activated with aluminium alkyls.

110 The preparation of masterbatch blends in accordance with the present invention will now be illustrated with reference to the following Examples 1 and 2.

115 EXAMPLE 1
 A sodium benzoate masterbatch was prepared by charging a vessel with 150 U.S.

gallons of isopropyl alcohol and adding to the alcohol three U.S. gallons of a saturated solution of sodium benzoate in water (2.08 gallons of water containing 10.58 pounds of sodium benzoate). The addition of the solution of sodium benzoate was carried out at room temperature (about 25°C) and was mixed. The result was a gel-like slurry. Following this (still at room temperature) there was added with admixing 10.58 pounds of polypropylene powder having the following particle size distribution:

	Mesh Size	Weight %
15	20	7.4
	40	20
	60	17.3
	80	9.3
	120	12.3
	Fines	33.7

20 The resulting powder-gel slurry was agitated to insure a good and thorough dispersion (the above procedure results in a 50 percent masterbatch of sodium benzoate and polypropylene). After the thorough mixing step, 25 the mixture was centrifuged and the cake was dried at 150°F under vacuum of about 30 inches of mercury.

It is highly desirable, in order to obtain a good distribution of the very fine particle 30 size sodium benzoate, to employ a finely divided polyolefin powder. Usually as a general rule, the finer the particle size, the better, and a preferred size is an average of around 200 mesh (50% above and 50% below) and lower. (Particle size is defined by ASTM D-1921-63 and is entitled "Particle Size (Sieve Analysis) of Plastic Materials".)

EXAMPLE 2

40 Following the procedure of Example 1, another nucleating agent/polyolefin masterbatch was prepared by adding 7.6 pounds of sodium benzoate to one and one half U.S. gallons of water and then adding this solution to seventy-five U.S. gallons of isopropyl 45 alcohol to obtain a gel as before of precipitated sodium benzoate with occluded and entrapped water and alcohol, the sodium benzoate being in finely divided form. This form 50 is stable at ambient temperatures and the salt does not readily settle out. The resulting gel was then processed as above to prepare a masterbatch by adding enough polypropylene powder to form a 50% masterbatch.

55 In accordance with another aspect of the invention the masterbatch is employed for introducing the nucleating agent into alpha-olefin polymers. For most commercial applications the polymer employed in the preparation 60 of the masterbatch will be the same as the polymer to which the masterbatch is added. However, the polymers may also be different,

since only minor amounts of the masterbatch need to be added in order to achieve the desired modification of physical properties. Thus the masterbatch may be prepared from any polymer compatible with the polymer to which it is subsequently added. For example masterbatches suitable for mixing with polypropylene may be prepared from copolymers of propylene with other olefins (block or random), polyethylene, polybutene and poly-4-methyl pentene-1. In general, the amount of polypropylene masterbatch employed assuming a 50% masterbatch will range from about 0.05% to 2.0%, and preferably from about 0.1% to 1.0% by weight based on the weight of the polypropylene polymer to which it is added. The amount of nucleating agent needed for the various crystalline polymers is from 0.05 to 0.2% by weight or higher, for example 1 percent.

Various methods can be employed for introducing the masterbatch of this invention into crystalline polymers. It is possible, for example, to add the masterbatch to a dry polypropylene polymer either when the polymer is in the form of a powder fluff or in the form of shaped pellets. Alternatively, the masterbatch can be added to the crystallizable polypropylene polymer after the latter has been melted.

In order to obtain desired improvements in physical properties it is essential that a substantially homogeneous distribution of the masterbatch in the molten polypropylene polymer be obtained prior to the final crystallization of the polymer. Mixing of the masterbatch and the polymer is best carried out by applying mechanical mixing at temperatures at which the polymer has a relatively low viscosity, i.e. a temperature exceeding the melting temperature of the polymer by from 20° to 150°C. These conditions are particularly important when products of greatly enhanced clarity of transparency are desired.

As a result of the treatment with the masterbatch, the molten polymer can be cooled rapidly or over a relatively long period of time to give a solid polymer product having a high degree of crystallinity and a fine spherulite structure.

Cooling of the polymer can take place in any suitable apparatus. Cooling is usually carried out in conventional apparatus associated with the production of shaped articles from olefin polymers.

The manner in which mixing takes place should provide a uniform distribution of the crystallization promoting additive in the polymer. This uniform distribution remains substantially unaffected during the crystallization, both when crystallization progresses very rapidly and when there is considerable temperature gradient, as in the cooling of large objects.

- Shaped articles formed from polymers to which the masterbatch has been added may be, for example, bars, sheets, films, tapes, granules, rods or flakes, moulded or extruded 5 large or small shapes or filament. Shaped articles according to this invention may be manufactured from the mixtures according to this invention by casting, compression moulding or injection moulding; films may be obtained by blowing or by slit extrusion; filaments, bars and tapes may be obtained by extrusion. If desired, these can be reduced by chopping, to the form of granules or chips. Filaments can be stretched to obtain further 10 improvement of properties.
- The incorporation of the masterbatch into alpha-olefin polymers in accordance with the invention will now be illustrated with reference to Example 3.
- EXAMPLE 3**
- Using a masterbatch prepared as in Example 1 an injection moulding polypropylene (melt index 10) containing from 2 to 3 percent ethylene as a random copolymer was nucleated by blending (melt) with sufficient masterbatch to result in a polypropylene containing 0.05 percent by weight sodium benzoate. The treated polymer had increased stiffness in comparison to the untreated material.
- In a similar manner to the above, a film grade propylene homopolymer having a melt index of about 5 and a boiling heptane insoluble content of about 95, was treated to obtain a product containing 0.05 percent sodium benzoate. Excellent results were obtained with respect to clarity and transparency due to the nucleation effect of the additive.
- WHAT WE CLAIM IS:—**
1. A masterbatch blend comprising from 40 95% to 25% by weight of a crystalline alpha-olefin polymer and, substantially uniformly dispersed therein, from 5% to 75% by weight of a water-soluble oxygen-containing nucleating agent.
 2. A blend as claimed in claim 1 comprising from 25% to 50% by weight of the nucleating agent.
 3. A blend as claimed in claim 1 or claim 50 50 comprising from 30% to 40% by weight of the nucleating agent.
 4. A blend as claimed in any one of the preceding claims containing an antioxidant, a stabiliser against ultraviolet radiation, a filler, a slip agent and/or an antistat.
 5. A blend as claimed in claim 1 comprising approximately 50% by weight of the alpha-olefin polymer and approximately 50% by weight of the nucleating agent.
 6. A blend as claimed in any one of the preceding claims wherein the alpha-olefin polymer is a homopolymer of ethylene, propylene, 4 - methylpentene - 1, butene - 1, 3 - methylbutene - 1 or pentene - 1, or a block copolymer of ethylene and another alpha-olefin or a random or block copolymer of propylene with ethylene, 4 - methylpentene - 1, 3 - methylbutene - 1 or pentene - 1.
 7. A blend as claimed in any one of the preceding claims wherein the nucleating agent is an aliphatic, aromatic or alkyl substituted aromatic monoc- or dicarboxylic acid or an alkali metal salt thereof or a mixture of such acids and/or salts.
 8. A blend as claimed in claim 7 wherein the nucleating agent is benzoic acid, sodium benzocate, lithium benzocate, sodium glutarate, lithium glutarate, sodium adipate, lithium adipate, sodium succinate, lithium succinate, sodium crotonate, t-butyl sodium benzoate, ortho methyl benzoic acid, 2, 4 - dimethyl benzoic acid, alpha naphthoic acid, trans cinnamic acid or an alkali metal salt of trans cinnamic acid.
 9. A process for preparing a masterbatch blend of a crystalline alpha-olefin polymer and, substantially uniformly dispersed therein, a water-soluble oxygen-containing nucleating agent, which process comprises dissolving the nucleating agent in water, precipitating a gel-like slurry by admixing the solution of the nucleating agent in water with an excess amount of a non-solvent, with which water is at least partially miscible, for the nucleating agent, adding particles of a crystalline alpha-olefin polymer to the slurry, agitating to disperse the polymer particles in the slurry, and separating the solids from the resulting polymer-containing slurry.
 10. A process as claimed in claim 9 wherein the nucleating agent is an aliphatic, aromatic or alkyl substituted aromatic monoc- or dicarboxylic acid or an alkali metal salt thereof or a mixture of such acids and/or salts.
 11. A process as claimed in claim 10 wherein the nucleating agent is benzoic acid, sodium benzocate, lithium benzocate, sodium glutarate, lithium glutarate, sodium adipate, lithium adipate, sodium succinate, lithium succinate, sodium crotonate, t-butyl sodium benzoate, ortho methyl benzoic acid, 2,4-dimethyl benzoic acid, alpha naphthoic acid, trans cinnamic acid or an alkali metal salt of trans cinnamic acid.
 12. A process as claimed in any one of claims 9 to 11 wherein the alpha-olefin polymer is a homopolymer of ethylene propylene, 4 - methylpentene - 1, butene - 1, 3 - methylbutene - 1 or pentene - 1, or a block copolymer of ethylene and another alpha-olefin or a random or block copolymer of propylene with ethylene, 4 - methylpentene - 1, 3 - methylbutene - 1 or pentene - 1.
 13. A process as claimed in any one of claims 9 to 12 wherein the solution of the nucleating agent in water contains the nucleating agent in an amount of at least 10% of the concentration of a saturated solution thereof.
 14. A process as claimed in claim 13 where-

- in the solution contains from 10% to 90% of the nucleating agent.
15. A process as claimed in any one of claims 9 to 14 wherein the non-solvent is an alcohol, ketone, ester or partial ester, glycol or aldehyde.
16. A process as claimed in claim 15 wherein the non-solvent is an alcohol containing from 1 to 10 carbon atoms.
- 10 17. A process as claimed in claim 15 wherein the non-solvent is methanol, ethanol, isopropanol, propanol, pentanol, hexanol or a mixture thereof or acetone or ethylene glycol.
- 15 18. A process as claimed in any one of claims 9 to 17 wherein the solution of the nucleating agent in water is admixed with 10 to 200 times its volume of the non-solvent.
19. A process as claimed in any one of 20 claims 9 to 18 wherein water is substantially completely miscible with the non-solvent.
- 20 20. A process as claimed in any one of claims 9 to 19 wherein the process is carried out under ambient temperature and pressure conditions or at a temperature of from 30° to 100°C.
21. A process as claimed in any one of 30 claims 9 to 20 wherein the solids are separated from the polymer-containing slurry in a drum filter or centrifuge.
22. A process as claimed in any one of 35 claims 9 to 21 wherein the solids separated from the polymer-containing slurry are dried at a temperature of from 20° to 60°C and a pressure of not more than 15 inches of Hg.
23. A process as claimed in any one of 40 claims 9 to 22 wherein the particles of crystalline alpha-olefin polymer have a size of not more than 20 mesh.
24. A process as claimed in claim 9 and substantially as hereinbefore described with reference to Example 1 or Example 2.
25. A blend of a crystalline alpha-olefin 45 polymer and a water-soluble oxygen-containing nucleating agent whenever prepared by a process as claimed in any one of claims 9 to 24.
26. A crystalline alpha-olefin polymer having a masterbatch blend as claimed in any one of claims 1 to 8 and 25 substantially homogeneously distributed therein. 50
27. A crystalline alpha-olefin polymer as claimed in claim 26 wherein the masterbatch blend is present in an amount to provide from 0.05% to 2.0% by weight of the nucleating agent. 55
28. A crystalline alpha-olefin polymer as claimed in claim 27 wherein the masterbatch blend is present in an amount to provide 0.1% to 1.0% by weight of the nucleating agent. 60
29. A process for preparing a crystalline alpha-olefin polymer as claimed in any one of claims 26 to 28, which process comprises melting a crystalline alpha-olefin polymer, mixing the masterbatch blend therewith and cooling the resulting mixture. 65
30. A process as claimed in claim 29 wherein mixing is carried out at a temperature of from 20° to 150°C greater than the melting temperature of the polymer. 70
31. A process for preparing a crystalline alpha-olefin polymer having a masterbatch blend substantially homogeneously distributed therein substantially as hereinbefore described with reference to Example 3. 75
32. A crystalline alpha-olefin polymer when prepared by the process claimed in any one of claims 29 to 31.
33. A shaped article formed from a crystalline alpha-olefin polymer as claimed in any one of claims 26 to 28 and 32. 80
34. Bars, sheets, films, tapes, granules, rods, flakes or filaments formed from a crystalline alpha-olefin polymer as claimed in any one of claims 26 to 28 and 32. 85

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.1.
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